Supporting Information

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UV-Dissipation Mechanisms in the Eumelanin Building Block DHICA**


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SUPPORTING INFORMATION

$^1$H NMR spectrum (acetone-$d_6$), 300 MHz
$^{13}$C NMR spectrum (acetone-d$_6$), 75 MHz, selected region
**Additional Figures**

Figure A. Normalized fluorescence decay kinetics at 460 nm of DHICA in 0.1 M pH 2.5 buffer, recorded at time range 2. The ingrowth is as fast as the time resolution (~ 5 ps).

Figure B. Normalized fluorescence decay kinetics at various wavelengths of DHICA in 0.1 M pH 7.0 buffer. The trace does not change any longer from 540 nm and longer wavelengths.

Figure C. Fluorescence decay kinetics at 380 nm and 540 nm of DHICA in 0.1 M pH 7.0 buffer, recorded at time range 2. Apart from a slow ingrowth, the trace at 540 nm also clearly consists of a fast ingrowth.
Estimation lifetime carboxylate anion without the presence of complex formation

The measured lifetime ($\tau_F$) depends on the radiative rate constant ($k_R$), the rate constant for non-radiative decay ($k_{NR}$) and the rate for complex formation ($k_C$) according to:

$$\tau_F = \frac{1}{k_R + k_{NR} + k_C}$$

(A)

In 0.1 M buffer, the measured lifetime of the carboxylate anion equals 1.1 ns, i.e.

$$k_R + k_{NR} + k_C = 9.1 \cdot 10^8 \text{ s}^{-1}$$

(B)

Lowering the molarity by a factor of 5 to 0.02 M reduces $k_C$ by a factor of $5^{2/3}$, reflected by a longer lifetime of 1.6 ns, which means that:

$$k_R + k_{NR} + \frac{k_C}{5^{2/3}} = 6.3 \cdot 10^8 \text{ s}^{-1}$$

(C)

Combination of equations 2 and 3 give $k_R + k_{NR} = 4.8 \cdot 10^8 \text{ s}^{-1}$. In the absence of complex formation, the lifetime equals $1/ 4.8 \cdot 10^8 = 2.1$ ns.